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REPORT DOCUMENTATION PAGE

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE	3. REPORT TYPE AND DATES COVERED FINAL REPORT 01 Apr 95 - 30 Sep 96	
4. TITLE AND SUBTITLE PREPARATION OF HIGH-PERFORMANCE FIELD EMISSION CATHODES BY DEPOSITION OF LOW WORK FUNCTION FILMS			5. FUNDING NUMBERS 61102F 2301/ES	
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9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NE 110 Duncan Avenue Suite B115 Bolling AFB DC 20332-8050			10. SPONSORING/MONITORING AGENCY REPORT NUMBER F49620-95-1-0299	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The results of the rather preliminary HfC film experiments on a Mo FEA do not suggest better performance than ZrC on Mo FEAs. However, we believe there is substantial hope for optimism. The study of ZrC and HfC films deposited onto macroscopic Mo substrates shows approximately the same work function for both systems, approximately 3.0 eV. Our earlier work with single crystal free-standing emitters of ZrC and HfC suggested an even lower ultimate work function for HfC than for ZrC, and an apparently better emission stability. We believe that further studies of deposited films of HfC onto field emitters would allow this lower work function to be realized there as well.				
14. SUBJECT TERMS			15. NUMBER OF PAGES	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT	

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**PREPARATION OF HIGH-PERFORMANCE FIELD EMISSION
CATHODES BY DEPOSITION OF LOW WORK FUNCTION FILMS
GRANT NO. F49620-95-1-0299**

**FINAL TECHNICAL REPORT
12/31/1996**

To

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Project Start Date

1 May 1995

Project End Date

30 September 1996

Project Amount

\$98,398

PREPARATION OF HIGH-PERFORMANCE FIELD EMISSION CATHODES BY DEPOSITION OF LOW WORK FUNCTION FILMS

I. INTRODUCTION

The requirement, under the Vacuum Electronics Initiative, for pre-bunched emission of electrons at high current density has stimulated a substantial amount of research in development of field emission array cathodes (FEAs). The materials chosen for the field emitters in FEAs developed so far have been Si (ease of fabrication) and Mo (ease of fabrication and refractory properties). Our earlier efforts under this initiative (DARPA Grant MDA972-91-J-1014 and AFOSR Grant AFOSR-91-0409) were to develop single, free-standing single crystal field emitters of materials with superior emission properties, including very high emitted current density, thermal stability, resistance to degradation in air, and long operational lifetime. The emitter materials which we have studied include ZrC, HfC, and TaC. These carbides have work functions of the order of 3.5 eV, approximately 1 eV lower than the commonly used field emission array cathode materials Mo and Si. They have excellent electrical conductivities and are also very stable, with high melting points and resistance to chemical attack.

We had also done a careful investigation of the surface properties of the particular carbide ZrC. Specimens in the form of bulk single crystals of chosen orientation were characterized as to work function, surface adsorption characteristics, and electron emission properties. We performed extensive studies of the field emission characteristics of individual, free-standing emitters fabricated from single crystal zone refined ZrC rod prepared in our laboratory. Both DC and pulsed measurements were made, and the effects of emitter preparation and operating conditions (including system vacuum) were investigated. We also studied vapor deposited films of ZrC on macroscopic Ta and W substrates and began a study of these films on prefabricated individual field emitters of W, Mo, and Si, and FEAs of Mo and Si emitters.

The purpose of the project on which we report here was to extend these efforts to include an investigation of low work function refractory HfC compound films on W, Mo and Si macroscopic substrates, and to extend the studies of ZrC on individual emitters of these materials and on FEAs with emitters of these materials. We hoped over the course of the originally proposed three-year program to extend the film studies on emitters and FEAs to include HfC films as well as ZrC films. However, the program was finally limited to a single year of funding, so the research effort needed to be restricted from that originally

proposed. However, we were still able to get some results for HfC film deposition onto individual field emitters and onto FEAs.

II. PROPERTIES OF HfC FILMS

The first task of the program was aimed at developing a more thorough understanding of the properties of films of the carbide HfC. Two ultrahigh vacuum (UHV) systems were used for this work. The first system contained a FERP¹ (field emission retarding potential) analyzer, capable of determining the absolute surface work function. Also contained on this system were a fixed beam Auger electron spectrometer, an Ar⁺ sputtering gun, a HfC evaporative source, and a special carousel stage. The second UHV system contained many of the same analytical components, fixed beam Auger, FERP, LEED, substrate holder, and a HfC evaporative source.

An e-beam heated, high purity HfC evaporation source was used to deposit the film layer. The HfC used was a single crystal prepared in our laboratory by arc float zone refinement.² The composition was checked by chemical analysis done in another lab, and by Auger electron spectroscopy (AES) in our lab to ensure HfC crystal purity. Deposition coverage of HfC was carefully studied by AES using a Ta ribbon as a substrate. The calibration of film thickness was done by keeping the bombardment current and the high voltage fixed and varying the deposition time. When the AES signal of the substrate fell below 1%, we assumed the coverage was approximately equal to three monolayers of film. The results were used as a guide for later HfC deposition onto various planar and field emitters substrates.

We analyzed the work functions of the films deposited onto Ta substrates using the FERP technique. This method yields an absolute work function value without adverse complications from high temperatures or high electric fields used in thermionic or field emission measurements. Subsequent data runs were completed and the results are shown in Fig. 1. These results show that a minimum work function of 2.8 eV is obtained after heating to approximately 700 K. As a check on the system, a clean polycrystalline Ta work function of 4.25 eV was obtained following extended thermal cleaning prior to dosing with a thin HfC film and again after the dose run as is shown in Fig. 1. This clean value is in agreement with published data and the surface cleanliness was checked by AES.

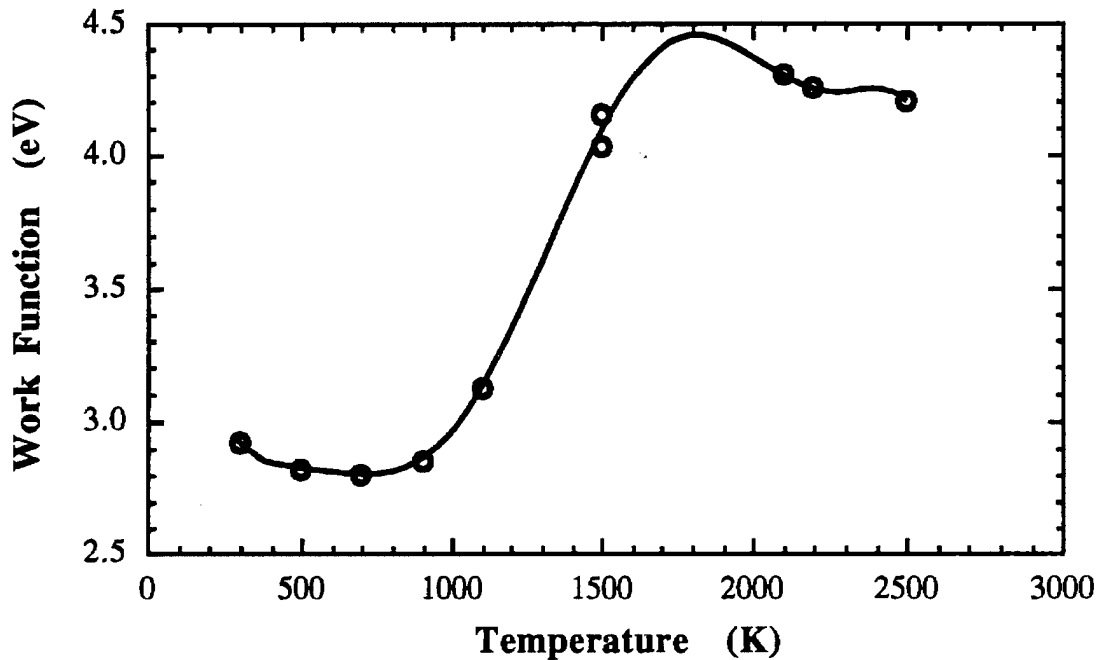


Fig. 1: Absolute work function measurements taken via the FERP technique. These data show the work function values directly after HfC deposition and at intervals after heating the Ta substrate to the temperatures indicated.

We then began a careful investigation of HfC deposited onto Mo substrates. A 12.5 μm thick Mo ribbon was used for this work. Initial measurements on a clean Mo surface (heated to >2000 K) gave a value of 4.6 eV which is in agreement with published data for clean polycrystalline Mo. Figure 2 shows the results obtained on the thickest HfC film deposition (≈ 10 nm) which we made. As can be seen, the lowest value of 2.85 eV is obtained after heating to 800 K.

As a prelude to deposition of HfC onto Si we next looked at a sapphire substrate with r-plane orientation. We could not heat this substrate, so only a single room temperature value was obtained following each deposition. We obtained a value of 2.7 eV for HfC on sapphire. We did not extend this investigation to a study of HfC on Si during this program. Instead, we chose to concentrate our efforts on the study of films deposited onto individual field emitters and field emitter arrays (FEAs), which we shall now describe.

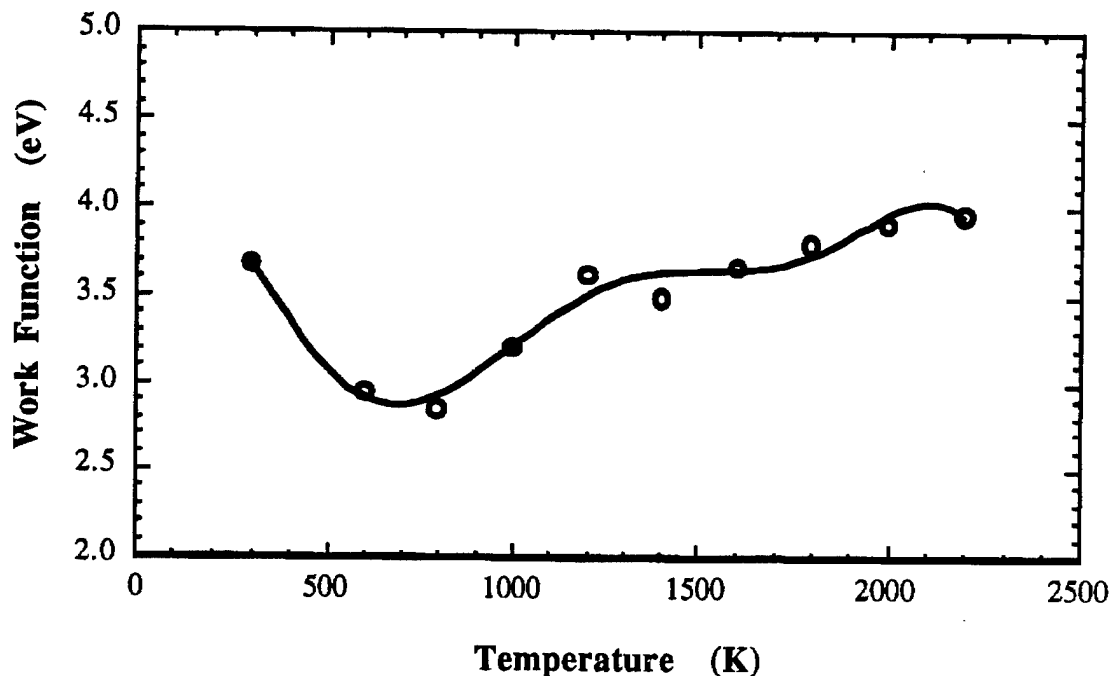


Fig. 2: Absolute work function measurements taken via the FERP technique. These data shows the values directly after deposition and at intervals after heating the substrate to the temperatures indicated.

III. CARBIDE FILMS ON FIELD EMITTERS

A. Individual, free-standing emitters

We had already observed high current density field emission, greater than 1×10^8 A/cm², from single crystal HfC and ZrC cathodes.³ Single crystal samples of these materials have work functions approximately 1 eV lower than W, Mo, or Si making them attractive candidates for low voltage microelectronic field emitter arrays (FEAs). By comparing HfC to ZrC, we had found HfC to have a lower work function by several tenths on an eV.^{4,5} However, in order to make these materials useful for practical arrays, it is necessary to be able to fabricate many identical field emitters from them. One possible way we saw to achieve this goal was to deposit carbide films onto prefabricated emitter arrays. The challenge with this approach was the achievement of the desired properties (stability and low work function) in the deposited layers. Therefore, we performed preliminary film deposition experiments on individual, free-standing emitters before beginning an investigation of film deposition onto FEAs.

The primary advantage of studies on individual, free-standing emitters is that these emitters are easy to prepare and to characterize. Using heating and field desorption techniques, it is

possible to prepare atomically clean and smooth emitters in the field emission microscope (FEM) and field ion microscope (FIM), with stable and reproducible I - V characteristics. Thus, deposition of the film can be made onto a well-understood substrate, comparable to the corresponding macroscopic substrate which has been characterized by surface analytical techniques. After deposition, the emitter with its deposited layer can be studied in the FEM and FIM as well, to determine whether the film itself smoothly coats the underlying emitter surface and whether it is free of adsorbed active impurity species.

The key technical questions we hoped to address in the individual emitter studies relate to the emission characteristics of the film-on-substrate emitters. Improvements in the I - V characteristics were considered to be of primary importance. However, we also wished to address important issues of lifetime and the nature of lifetime-limiting mechanisms. The ability of the emitter to survive exposure to air (simulating shelf life) and then be able to perform satisfactorily is of great practical importance, and we hoped to address this issue as well.

Previous research had dealt exclusively with the use of ZrC films to change the emission properties of planar surfaces, single field emitters, and field emitter arrays.⁶ Benefits from these overcoatings have been lower planar surface work functions (e.g. 1 eV work function lowering from clean surfaces for Mo and Ta), reduced work function and beam confinement when deposited on single emitters of W or Mo, and a marked reduction of turn-on voltages when deposited on FEAs of Mo⁷ and Si⁸. We report here on the results of this program, where we undertook an investigation of HfC films and overcoatings on field emitters.

We began by deposition of HfC onto a carefully prepared individual W or Mo field emitter, and measured changes in $I(V)$ characteristics. A UHV system was configured with the appropriate carbide evaporative source, a field emitter holder, and a phosphor screen to view emission and obtain $I(V)$ data. The single emitters used in this study were individually fabricated via electrochemical etching of polycrystalline wire, which generally has a natural (110) orientation. The W and Mo emitters were etched in sodium hydroxide and phosphoric acid solutions respectively.

In practice, each single emitter was tested by a series of separate steps. The emitter was first cleaned by heating up to about 1900 K (Mo) or 2100 K (W) and field emission microscopy (FEM) was used to verify the crystal orientation and condition of the emitter

apex. The idea here was to chose a temperature at which the emitters could be cleaned without being blunted too much. After a clean tip was obtained, an $I(V)$ data run was taken and was immediately followed by HfC film deposition. Usually, the deposited HfC film was a few monolayers thick. The film was then subjected to a variety of heating treatments. After each treatment, FEM was used to examine the tip and $I(V)$ data were obtained. Figure 3 compares the $I(V)$ for a tungsten single field emitter. The observed lower turn-on voltage for the dosed tip seems to indicate that the work function of the dosed tip has lowered significantly.

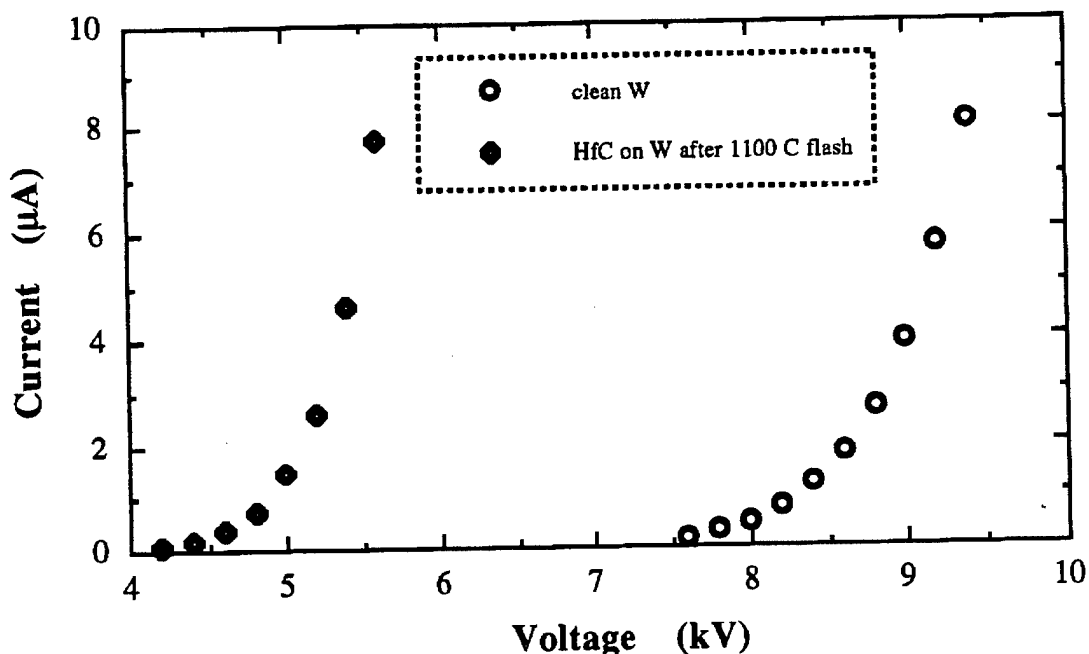


Fig. 3: $I(V)$ data from a crystalline tungsten, single field emitter. The $I(V)$ characteristics of the clean and HfC-covered W emitter surface are shown. After deposition, the emitter was heated to 1100 K before the data were taken.

The cleaning and film deposition procedure discussed above was carried out for a Mo single crystal emitter. Figure 4 shows $I(V)$ data for the clean Mo emitter and for the HfC coated surface which exhibits a 53% reduction of the turn-on voltage. Figure 5 is a Fowler-Nordheim plot showing the associated slopes developed from a least squares fit.

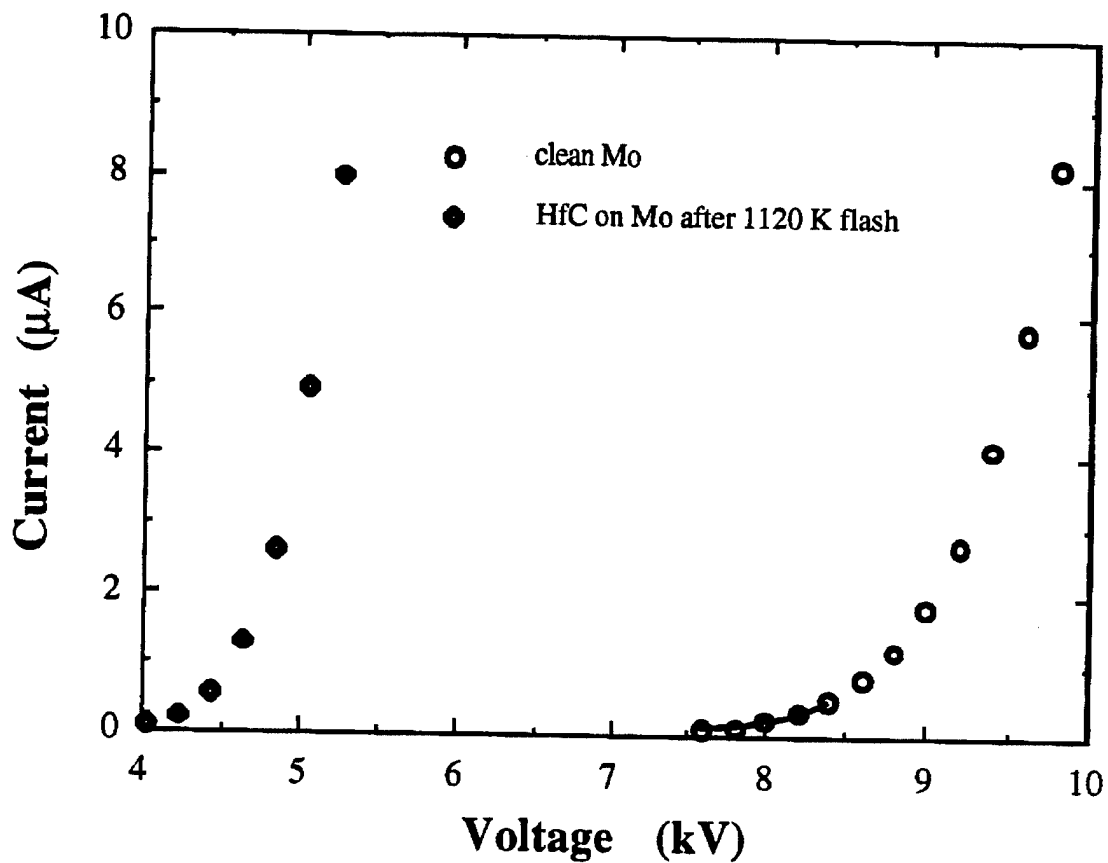


Fig. 4: $I(V)$ data from a crystalline Mo single field emitter. The $I(V)$ characteristics of the clean and HfC-covered Mo emitter surface are shown. After deposition, the emitter was heated to 1150 K before the data were taken.

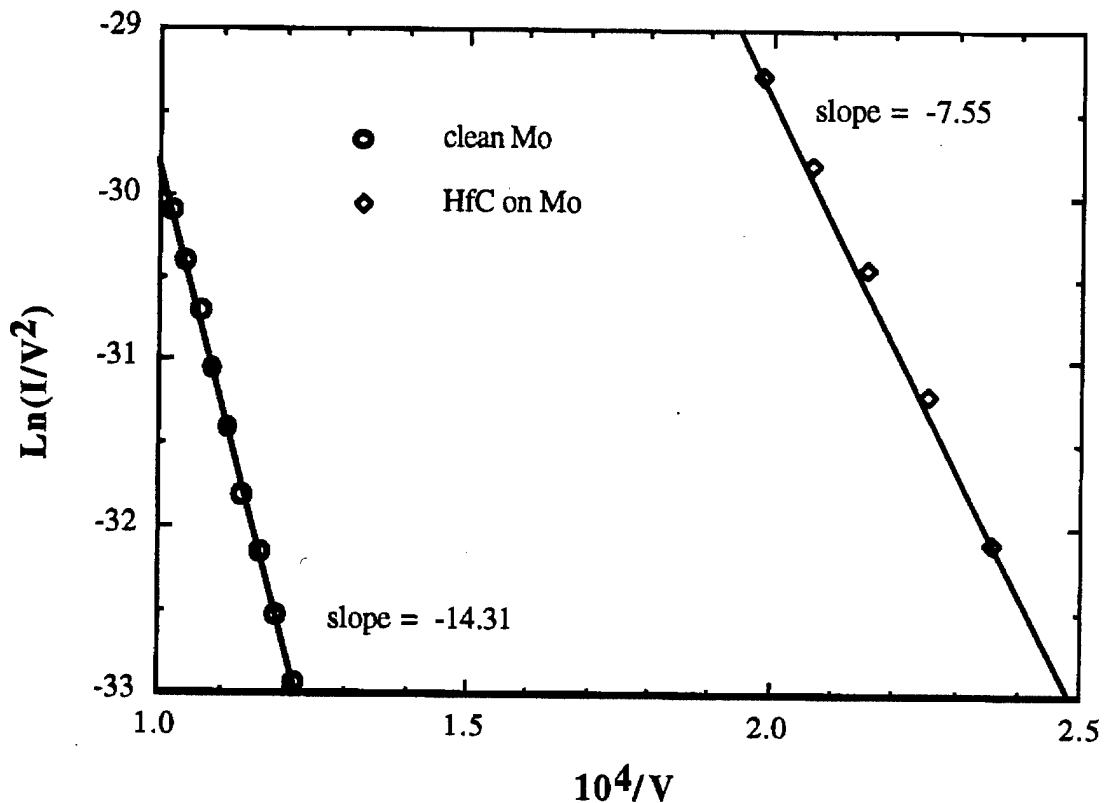


Fig. 5: Fowler-Nordheim curve from a single Mo field emitter. Both the clean and HfC-covered emission data are shown. After HfC deposition, the emitter was heated to 1120 K before the data were taken.

The results of these experiments are shown in Table I along with data previously taken with ZrC films. The work function ratio is calculated as follows: the slope of the Fowler-Nordheim (F-N) curve from an emitter with a carbide film is divided by the F-N slope from the clean cathode and the result is taken to the power two-thirds. This calculation gives a factor equal to the ratio of coated to clean work functions assuming an unchanging radius or β -factor. During the deposition of ZrC films, the work function was lowered and in most cases, the tip radius was increased slightly.⁶

Table I: Results of ZrC and HfC Film Deposition on Single Emitters

Film type & Substrate	Voltage Reduction @ same current	Work Function Ratio from F-N	Work Function Clean (eV)	Work Function with Film (eV)
ZrC/W	38%	0.78	4.52	3.54
ZrC/Mo	56%	0.64	4.60	2.95
ZrC/Si	27%	0.87	4.82	4.19
HfC/W	60%	0.65	4.52	2.94
HfC/Mo	53%	0.65	4.60	2.99

The increased emission at lower turn-on voltages is brought about by a work function lowering and not brought about by a change in tip radius for the case of HfC on Mo. To demonstrate this, we construct a plot of the Fowler-Nordheim slope vs intercept.⁹ Since the slope and intercepts are both functions of ϕ and β , we can plot a family of curves corresponding to constant β and a similar family of curves corresponding to a constant ϕ . These curves do not form an orthogonal set since it is not strictly possible to separate these two parameters. Shown in Fig. 6 are these families of curves as well as data points corresponding to field emission from clean Mo and Mo with a HfC film overlayer. This method of data comparison indicates that the reduction in turn-on voltage was derived from a work function reduction and that the tip radius change (change in β) was virtually zero.

B. Field emitter arrays (FEAs)

The study of carbide film evaporation onto FEAs was performed on two types of field emission array cathodes. The first cathode studied was a 10 x 10 array of Mo emitters in approximately 1 μm diameter apertures on 8 μm centers, supplied to us by SRI.⁷ The cathode was first operated in our vacuum system for several days until it had achieved essentially the same $I(V)$ characteristics which Spindt had observed before the cathode was shipped. Then the array was turned off and a ZrC deposit of approximately 3 atomic layers thickness was made. It was essential to calibrate the deposition very carefully in order to assure that a significant deposit was made, but that its thickness was not so great that the grid apertures were decreased appreciably.

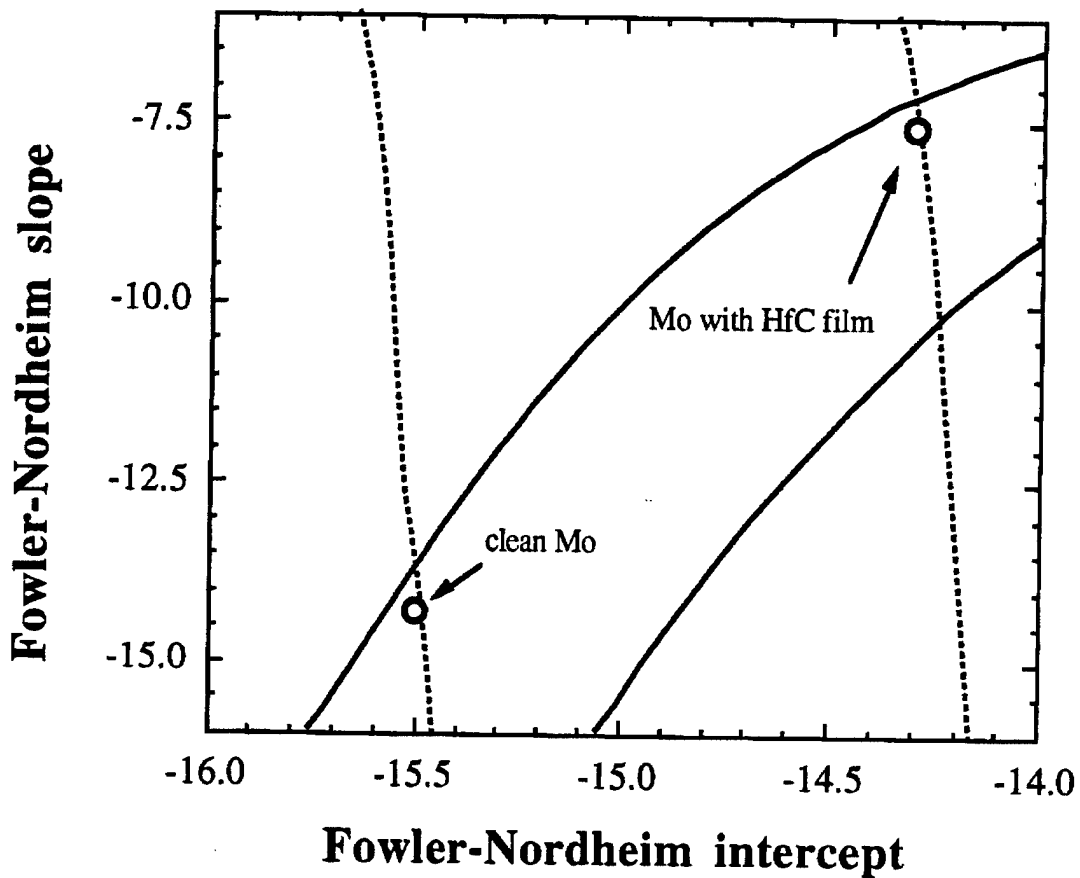


Fig. 6: Plotting Fowler-Nordheim slopes versus intercepts generates families of curves for constant ϕ , dashed lines, and constant β , solid lines. Superimposed on this are data from a smooth Mo emitter before and after deposition of a HfC thin film, solid circles. Note, these data indicate a work function lowering and an unchanged tip radius.

These experiments differed from the individual emitter experiments in several ways. First, the emitters in the array could not be cleaned by heating in the vacuum system. The only cleaning occurred during system bakeout and during operation of the cathode, which may have caused some local heating at the tips of the emitters. Second, the deposited layer could not be heated to form a single crystal structure, for the same reason. (In general, it is possible to heat these arrays to 500-700 °C without damage.) Finally, FEM images could not be obtained for individual emitters in the array, so it was not possible to rule out microscopic protrusions in the ZrC deposited layer on the emitter surface by direct observation of the emission pattern.

Studies were also made on a cathode which consisted of a 1100 tip close-packed array of Si emitters in approximately 4 μm diameter apertures on 8 μm centers, supplied by MCNC.⁸ Again this cathode could not be heated in our present system configuration. Depositions were made in a similar manner to those on the SRI cathode.

Results of the studies on these array cathodes are striking. Figure 7 shows a comparison of $I(V)$ data for the SRI cathode before deposition, after deposition for a total of 60 sec, after deposition for a total of 90 sec, and after operation for 30 hours following the 90 sec deposition. Note that a decrease of operating voltage from 122V to 68V for 100 μA emission current is observed following the 90 sec ZrC deposition, and even after 30 hours of operation the voltage yielding 100 μA emission has increased to only 78V. The ratio of Fowler-Nordheim slope for the ZrC layer to that for the cathode before deposition was approximately 0.68.

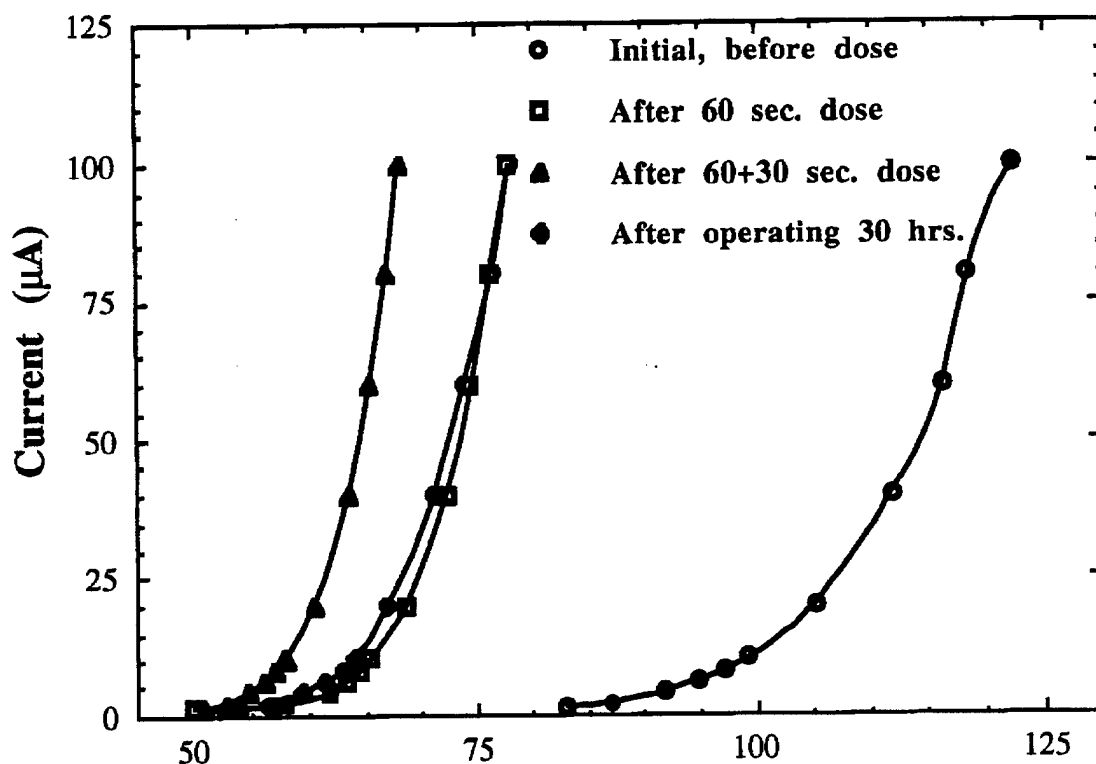


Fig. 7: $I(V)$ characteristics of SRI array cathode after achievement of initial stable operation, after ZrC deposition for 60 seconds and for 90 seconds total, and after operation for 30 hours following ZrC deposition.

The results for the MCNC cathode are not as well defined. We had trouble in depositing the ZrC film to the desired thickness, for two reasons. First, on two occasions the emitter and gate were found to have excessive leakage between their contacts after deposition and $I(V)$ data were unattainable. Second, the mounting of these arrays caused problems in the evaporation process. Finally, we were able to obtain the data shown in Figure 8. These results show the $I(V)$ characteristics of an MCNC array cathode after achievement of initial stable operation and after ZrC deposition for only 15 seconds. Further study was undertaken with an MCNC array mounted in a different manner, but this study was not completed during this program.

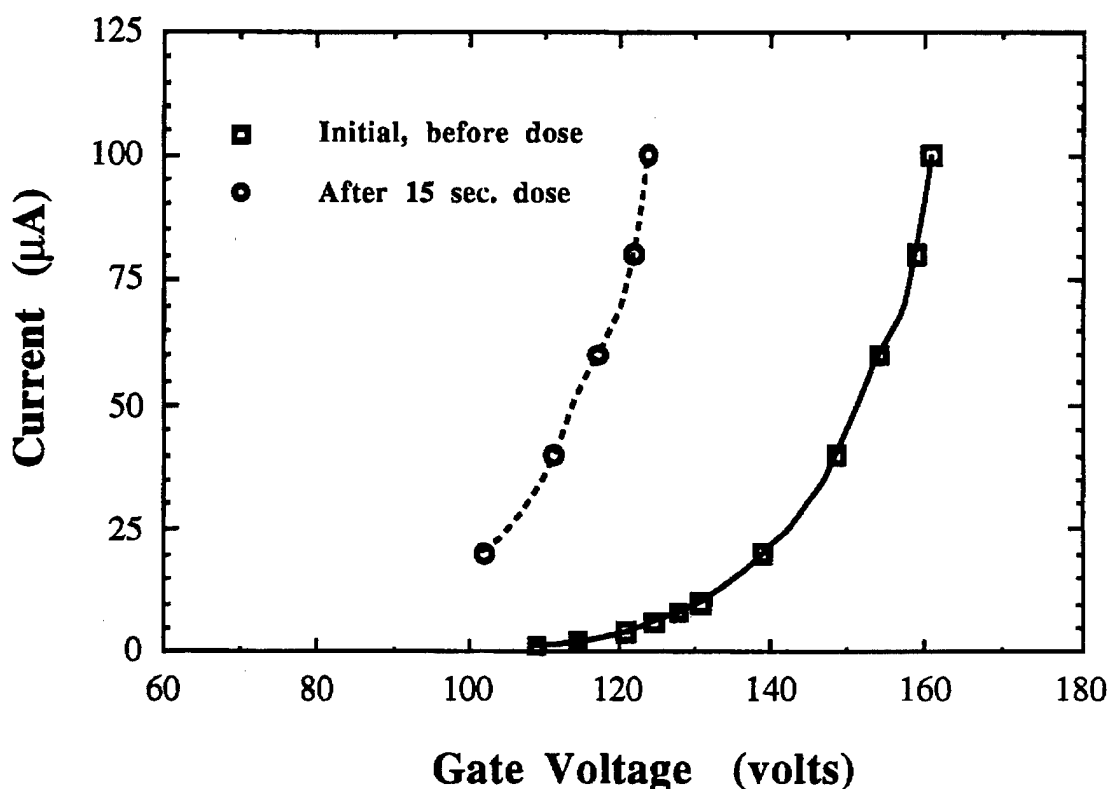


Fig. 8: $I(V)$ characteristics of MCNC array cathode after achievement of initial stable operation and after ZrC deposition for only 15 seconds.

Again we applied the analytical Fowler-Nordheim intercept *versus* slope technique to judge the mechanism of change. The results for the SRI cathode, shown in Fig. 9, comparing values before deposition and after the deposition plus 30 hours of operation, suggest a substantial decrease in work function plus a slight decrease in field enhancement factor (that is, a slight increase in emitter radius). These results are similar to those observed with the

individual Mo and W emitters when evaluated in this way, but here we are seeing the average over 100 emitters.

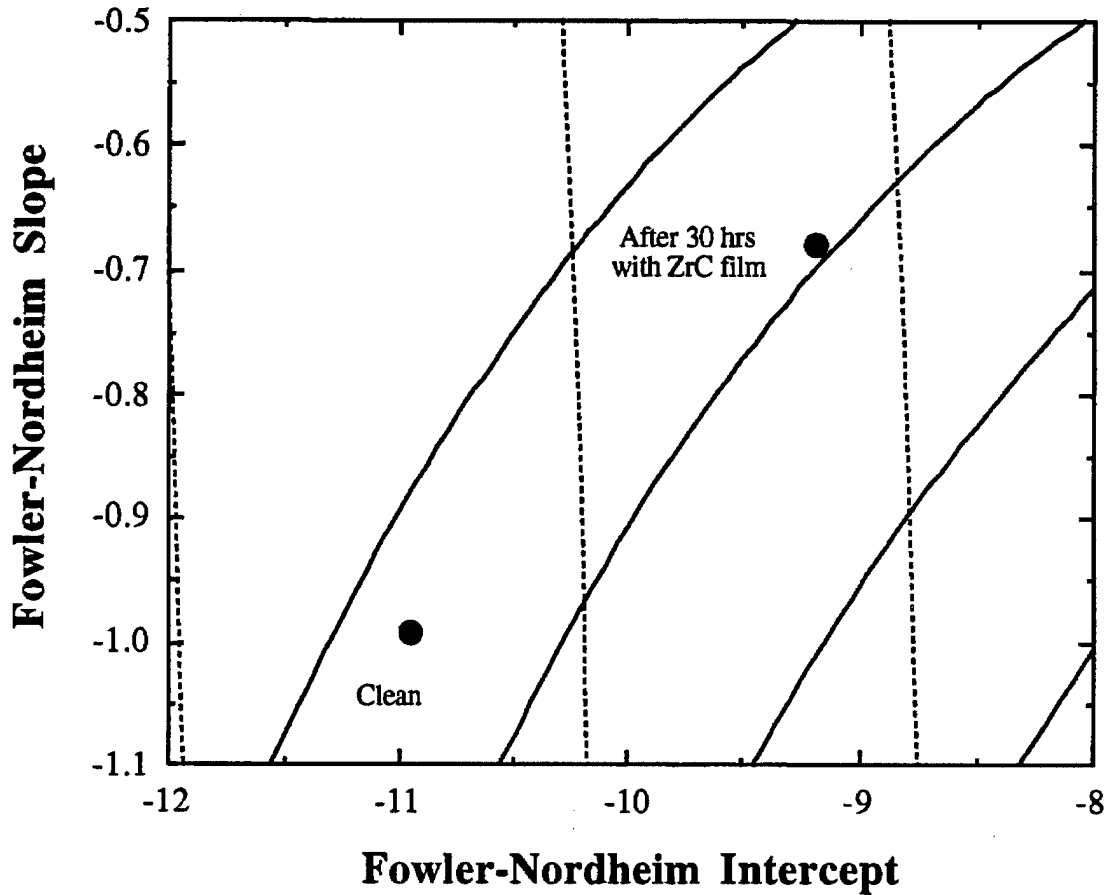


Fig. 9: Fowler-Nordheim slope versus intercept plot. This indicates that the lowering of the turn-on voltage associated with the ZrC film is due primarily to a reduction in the work function.

We were also able to perform a single experiment involving HfC deposition onto a Spindt-type FEA with Mo emitters. The results are shown in Table II, along with the results of the experiments just described. The limitation time available for this aspect of the research did not allow us to pursue studies of HfC deposition onto FEAs. We expect that with additional development, film depositions onto FEAs would produce results as promising as the results of depositions onto individual emitters already discussed.

Table II: Results of ZrC and HfC Film Deposition on FEAs

Film type & Substrate	Voltage Reduction @ same current	Work Function Ratio from F-N	Work Function Clean (eV)	Work Function with Film (eV)
ZrC/Mo FEA	44%	0.77	4.60	3.58
ZrC/Si FEA	~23%	~0.65	4.82	~3.15
HfC/Mo FEA	39%	0.88	4.60	4.02

The results of the rather preliminary HfC film experiments on a Mo FEA do not suggest better performance than ZrC on Mo FEAs. However, we believe there is substantial hope for optimism. The study of ZrC and HfC films deposited onto macroscopic Mo substrates shows approximately the same work function for both systems, approximately 3.0 eV. Our earlier work with single crystal free-standing emitters of ZrC and HfC suggested an even lower ultimate work function for HfC than for ZrC, and an apparently better emission stability. We believe that further studies of deposited films of HfC onto field emitters would allow this lower work function to be realized there as well.

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6. Tianbao Xie, W.A. Mackie, P.R. Davis, "Field emission from ZrC films on Si and Mo single emitters and emitter arrays," *J. Vac. Sci. Technol. B* **14**, 2090 (1996).
7. Spindt-type field-emission array obtained from Capp Spindt, SRI International, Menlo Park, CA 94025.
8. Silicon tipped FEAs obtained from Chris Ball and Dev Palmer, MCNC, P.O. Box 12889, Research Triangle Park, NC 27709.
9. J. Ishikawa, H. Tsuji, Y. Gotoh, T. Sasaki, T. Kaneko, M. Nagao, and K. Inoue, *J. Vac. Sci. Technol. B* **11**, 403 (1993).

V. PUBLICATIONS AND PRESENTATIONS DURING THE PROGRAM

A. Publications

P. R. Davis, W. A. Mackie and Tianbao Xie, "An investigation of the field emission characteristics of W, Mo and Si emitters with deposited ZrC films," in 1995 Vacuum Electronics Annual Review (Palisades Institute for Research Services, Inc.).

Tianbao Xie, W.A. Mackie, P.R. Davis, "Field emission from ZrC films on Si and Mo single emitters and emitter arrays," *J. Vac. Sci. Technol. B* 14, 2090 (1996).

Tianbao Xie, W.A. Mackie, P.R. Davis, "Emission characteristics of ZrC and HfC films field emitters," Vacuum Electronics Annual Review Abstracts (Naval Postgraduate School, 1996).

W. A. Mackie, Tianbao Xie, J. E. Blackwood, S. C. Williams and P. R. Davis, "Hafnium carbide films and film-coated field emission cathodes," *J. Vac. Sci. Technol. B* (submitted).

B. Presentations

Tianbao Xie, W.A. Mackie, P.R. Davis, "Emission characteristics of ZrC and HfC films field emitters," Vacuum Electronics Annual Review (Naval Postgraduate School, Monterey, CA, May 21-23, 1996).

Tianbao Xie, W. A. Mackie, and P. R. Davis, "Field emission from ZrC films on Si and Mo single emitters and emitter arrays," International Vacuum Microelectronics Conference, (Portland, OR, July 31-August 3, 1995).

P. R. Davis, W. A. Mackie and Tianbao Xie, "An investigation of the field emission characteristics of W, Mo and Si emitters with deposited ZrC films," (International Conference on Plasma Science, Madison, WI, June 5-8, 1995).

W. A. Mackie, Tianbao Xie, J. E. Blackwood, S. C. Williams and P. R. Davis, "Hafnium carbide films and film-coated field emission cathodes," (International Vacuum Microelectronics Conference, St. Petersburg, Russia, July, 1996), presented by F. M. Charbonnier.